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# On the Theory of Indicators and the Reactions of Phthaleins and Their Salts

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## DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF  
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY  
WITH THE REQUIREMENTS FOR THE DE-  
GREE OF DOCTOR OF PHILOSOPHY

BY  
EDGAR APPLE SLAGLE  
BALTIMORE

An oval-shaped stamp from the University of California, with the text "UNIVERSITY OF CALIFORNIA" and "BY" visible.

1909

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Especially does he wish to express his sincere gratitude and thanks to Associate Professor Acree, under whose personal direction this investigation has been pursued.



# On the Theory of Indicators and the Reactions of Phthaleins and Their Salts

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The rapid advance in our knowledge of the constitution and reactions of colored compounds of the aromatic series has made it clear that we must seek the cause of the manifestation of color in some deep-seated change in the molecule itself. The view formerly held that the color of these particular benzene derivatives is a function only of the increase in the molecular weight, or depends upon the introduction of certain elements or groups which tend to produce color, has long been abandoned.

The first important attempt to formulate a theory of color is seen in the hypothesis of O. N. Witt,<sup>1</sup> brought out in 1876, in which he assumed in all colored compounds the presence of certain specific groups (nitro, azo, cyan, etc.) which were thought to be responsible for the color. Witt called these groups *chromophores*. He recognized in some cases the additional influence of certain salt-forming groups (hydroxyl, amino, etc.) which intensify the color of the chromophore

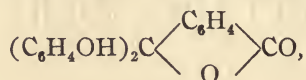
<sup>1</sup> Ber. d. chem. Ges., 9, 522.

and give to the compound the properties necessary in making the dye practically useful. These latter groups were called *auxochromes*.

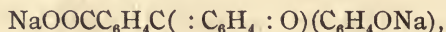
The quinone theory was first advanced by E. and O. Fischer to explain the colors of the dyestuffs of the rosaniline series and is really an extension of Witt's, which gives a more definite meaning to the term *chromophore*.

In 1889 Nietzki<sup>1</sup> extended the quinone theory, using, however, the modern formula of quinone, to the indamine and azine series. This conception was shortly after extended by Armstrong to include all colored compounds of the aromatic group.

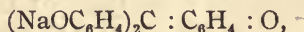
In 1893 Friedländer<sup>2</sup> assigned a corresponding quinone structure to phenolphthalein salts. He accepted Baeyer's formula for phenolphthalein in the free condition,



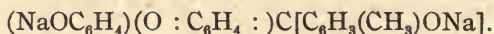
but assumed that an intramolecular change takes place in the molecule in the presence of alkalies which results in the formation of the colored quinone salt,



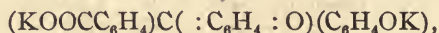
which he assumed to be analogous to the salts of aurin,



and of rosolic acid,



As a proof of the existence of the quinone structure in the salt



he prepared an oxime by treating an alkaline solution of phenolphthalein with hydroxylamine. Friedländer also suggested that phenolphthalein is a dibasic acid and that the salts are dibasic salts, but it remained for Meyer and Spengler<sup>3</sup> to prove

<sup>1</sup> Organische Farbstoffe, 1st Edition, p. 2.

<sup>2</sup> Ber. d. chem. Ges., **26**, 172.

<sup>3</sup> Ibid., **38**, 1318.

this by isolating and analyzing the salt  $C_{20}H_{12}O_4Na_2$ . At about the same time Bernsthen<sup>1</sup> came to similar conclusions in his researches on rhodamine 6 G and suggested that fluorescein exists in the free condition as the lactone compound but has the quinone structure in its salts.

A few years ago another conception of the cause of color was advanced by Baeyer<sup>2</sup> and called by him *halochromy*. He assumed the existence, in colored bodies of the triphenylmethane series, of a peculiar form of valence represented by a wavy bond,  $C \sim Cl$ , which Baeyer and Villiger called the *carbonium valence*. In this condition carbon was assumed to act as a strongly basic element which brings about the manifestation of color. This theory has recently been given up by Baeyer.

In 1890 Ostwald<sup>3</sup> proposed an explanation of color changes based on the theory of electrolytic dissociation. He assumed phenolphthalein to be an extremely weak acid and consequently but little dissociated; on the addition of an alkali a salt is formed which is largely dissociated, and the red color was thought to be due to the anion. The work on the physical constants of phenolphthalein has shown that a close quantitative relationship exists between Ostwald's theory and color change, yet many facts make it evident that this theory is in itself not able to account for all of the known phenomena. While it is true that the negative ions are colored, the change in color is due to a change in constitution of the compound, the ions having a structure different from that of the mother substance.

In 1903 Stieglitz<sup>4</sup> published a valuable article on the theory of indicators. By the use of (a) the evidence on the quinone theory furnished by Friedländer and Nietzki, (b) Hantzsch's ideas and equations concerning pseudoacids, and (c) Ostwald's conception of the quantitative relationships in the indicator work, Stieglitz came to the conclusion, in con-

<sup>1</sup> Chem. Ztg., 1892, 1956.

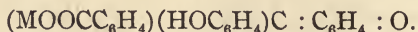
<sup>2</sup> Ber. d. chem. Ges., 38, 570, 1156.

<sup>3</sup> Lehrbuch der allgemeinen Chemie, 1891, p. 462; Scientific Foundations of Analytical Chemistry, 1890.

<sup>4</sup> J. Am. Chem. Soc., 25, 1112.



sidering phenolphthalein, that (p. 1115) "its red salts are the salts of a carboxylic acid, *not a phenol*, and have the constitution



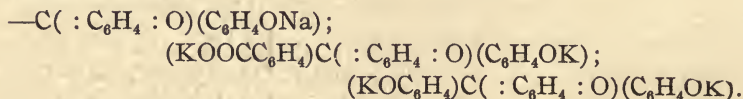
*The strongly chromophoric quinoid complex ( $:\text{C}_6\text{H}_4:\text{O}$ ) gives us an explanation of the production of intense color, which is entirely adequate in view of the laws governing color in organic compounds."* After developing the equation

$$C_Q \times C_H = K'' \times C_{LH}$$

for the affinity constant of the phenolphthalein he stated (p. 1122) that "its tendency to produce *the red color (the red salt)*<sup>1</sup> is measured by the same constant  $K''$ ." Hantzsch<sup>2</sup> points out that he too had proposed this theory.

In 1905 Meyer and Spengler<sup>3</sup> published a very important article in which they showed that the colored salts of phenolphthalein are dibasic salts, but they discarded the quinone hypothesis and accepted Baeyer's theory of halochromy.

In May, 1906, Acree and Brunel<sup>4</sup> began an investigation on indicators as a part of their work on tautomerism. It was seen by them that previous theories did not account fully for either the color phenomena or the alkylation reactions of aurin, phenolphthalein, fluorescein, etc., and they began work on these substances from the point of view that the tautomeric mono- and dibasic phenol and carboxyl salts are concerned in the alkylation reactions and in the color phenomena. It was seen, for instance, as had already been surmised by Friedländer,<sup>5</sup> that *the chief source of color in the salts of aurin, phenolphthalein, etc., is not the quinone group assumed by practically all of the other workers, but a quinone-phenolate group*,



<sup>1</sup> All the italics and words in parentheses are mine for emphasis.

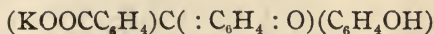
<sup>2</sup> Ber. d. chem. Ges., **39**, 1090. Rohland: *Ibid.*, **40**, 2172.

<sup>3</sup> *Ibid.*, **38**, 1318.

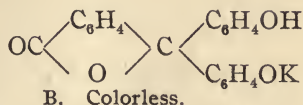
<sup>4</sup> Amer. Chem. J., **37**, 71. See also *Ibid.*, **27**, 118; **31**, 185; **32**, 606; **37**, 361; **38**, 1; **39**, 124, 226; Ber. d. chem. Ges., **35**, 553; **36**, 3139; **37**, 184, 618; **41**, 3199.

<sup>5</sup> Ber. d. chem. Ges., **26**, 172.

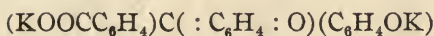
It was clear that the four possible mono- and dibasic salts, A, B, C and D, must be represented as follows:



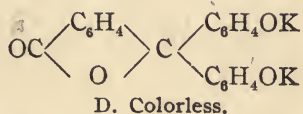
A. Faintly colored.



B. Colorless.

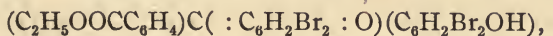


C. Deeply colored.

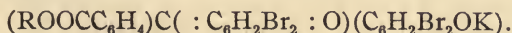


D. Colorless.

The compound A, assumed by others to be the colored salt of phenolphthalein, can give only faintly colored solutions, the carboxylphenoldibasic salt, C, being the salt really chiefly responsible for the color changes. B and D were thought to be colorless, as are the corresponding esters. This was perfectly apparent from the work of Nietzki and Burckhardt and Schroeter<sup>1</sup> on the fluorescein and phenolphthalein derivatives, and from the long known work on rosolic acid and aurin, which was pointed out by Friedländer; but the significance of these facts was unfortunately entirely overlooked by the other workers who referred to these articles, a fact which shows that even the most brilliant human minds are very imperfect instruments for aiding us to interpret nature's phenomena. The faintly colored carboxyl ester of tetrabromphenolphthalein, which is already a quinone,

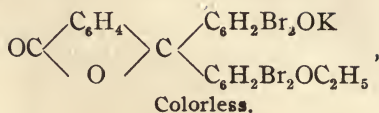
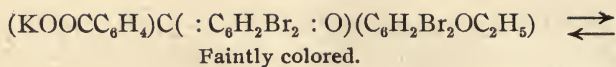


forms a deeply colored blue potassium or silver salt,

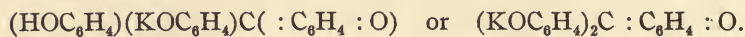


On the other hand, the isomeric phenol ester, which according to the quinone theory should yield deeply colored salts, gives practically colorless salts,

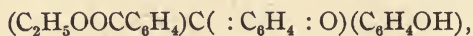
<sup>1</sup> Ber. d. chem. Ges., **28**, 48; **30**, 178.



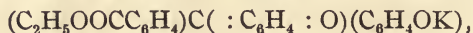
because no quinonephenolate group can be formed. Especially, though, was this point made clear by the properties of aurin,  $(\text{HOC}_6\text{H}_4)_2\text{C}(:\text{C}_6\text{H}_4:\text{O})$ . This compound has already a quinone group, and yet when alkali is added to an aqueous solution of the substance there is formed an intensely colored salt,



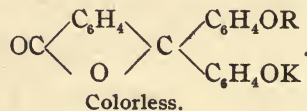
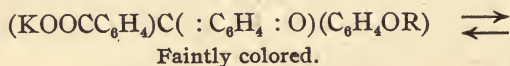
These reactions were sufficient to show that the quinone theory alone can not account for the color phenomena. This view has been recently confirmed more fully by the fact observed by Green and King<sup>1</sup> that the faintly colored carboxyl ethyl ester of phenolphthalein, itself a quinone derivative,



yields the intensely colored *quinonephenolate salt*,



whereas the isomeric phenol ethyl ester of phenolphthalein, which *can* form a quinone, but not a quinonephenolate, yields a colorless salt:

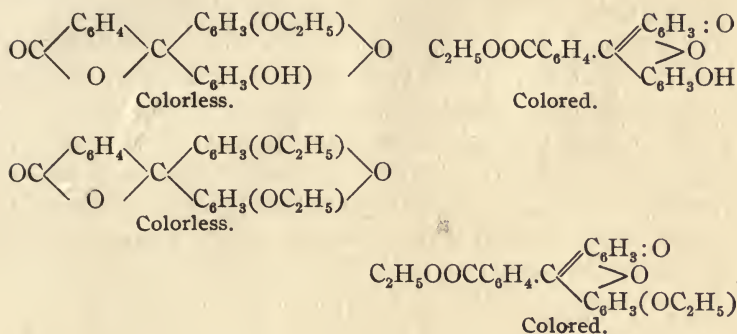


The evidence is just as strong that both phenol and carboxyl salts must be concerned in the alkylation reactions. Nietzki and Schroeter found that their "Fluorescein Kalium" and ethyl bromide gave the isomeric colorless phenol and col-

<sup>1</sup> Ber. d. chem. Ges., 40, 3724.

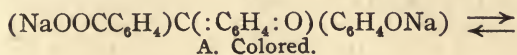


ored carboxyl monoethyl esters, and the isomeric colorless diphenol diethyl ester and colored carboxylphenol diethyl ester:

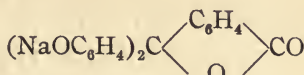


These esters seemed from the description given to be stable compounds which did not rearrange, and from Acree's theory of tautomeric compounds it seemed hardly likely that they were formed from tautomeric monobasic salts, but altogether probable that they were obtained from tautomeric dibasic fluorescein salts. Likewise alkylation experiments by Haller and Guyot<sup>1</sup> and by Herzig and Meyer<sup>2</sup> with phenolphthalein salts yielded 85 to 90 per cent of the colorless lactone dimethyl ester, whereas Orndorff<sup>3</sup> found that gallein yields both quinone and lactone esters.

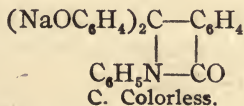
Both the color phenomena, then, and the alkylation reactions pointed to the presence and reactions of tautomeric dibasic salts:



A. Colored.



B. Colorless.



<sup>1</sup> Compt. Rend., **120**, 296.

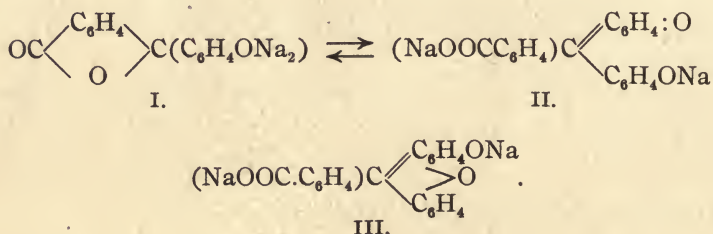
<sup>2</sup> Ber. d. chem. Ges., **28**, 3253.

<sup>3</sup> Am. Chem. J., **31**, 97.



Acree and Brunel believed that A is intensely colored, but that salts analogous to B are colorless, just as the corresponding salts of the anilides,<sup>1</sup> C, are without color. But they thought that by "Fluorescein Kalium" Nietzki and Schroeter perhaps meant the *monopotassium* salt, and if this had been true it would have been very unfortunate for their theory. They accordingly ordered some "Fluorescein Kalium" from Hoeschst and Company and the analysis proved that it contained more than 3 atoms of potassium to one molecular quantity of the salt. There was evidently, therefore, justification for a continuance of the problem from their point of view of tautomeric salts, but the work was given up on account of the departure of Dr. Brunel from this laboratory.

In the meantime, other work was appearing which had a very direct bearing on this problem. From a large number of investigations it appeared probable that we might have not only the quinoid and lactoid dibasic salts concerned in the colors, but also still another tautomeric salt, an intramolecular condensation product of the phenol salt with the carbonyl of the quinone group, which indeed seemed to be the chief source of color in such compounds:

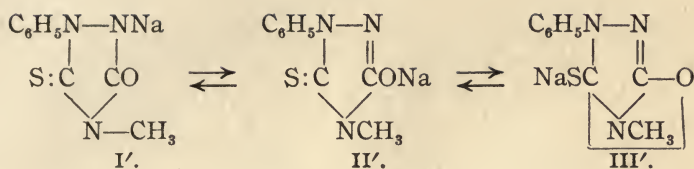


In work begun in 1902, Acree<sup>2</sup> obtained evidence that the 1-phenyl-3-oxy-4-methyl-5-thiourazole and its salts could exist not only in the two tautomeric forms, I'. and II', ordinarily assumed, but also in still another intramolecular form, III', analogous to III.:

<sup>1</sup> Meyer and Spengler: Ber. d. chem. Ges., **36**, 2949.

<sup>2</sup> Am. Chem. J., **31**, 187; **32**, 606. Nirdlinger: Dissertation, Johns Hopkins University, 1909.

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Busch and Opfermann<sup>1</sup> later actually isolated the corresponding 1,4-diphenyl-5-thiourazole acids, and Busch and Reinhardt<sup>2</sup> showed that the salts can exist. Acree and Nirdlinger have now made these tautomeric salts and actually proved quantitatively that one of them has the properties expected of a compound having the structure III'. Although these salts are not visibly colored yet they will without doubt be found to have different colors outside the visible spectrum, as do many other such compounds (Baly, Hardley, Keyser, etc.). The actual isolation of III'. proves the possible existence of the analogous substance III., and as long ago as 1904<sup>3</sup> it was pointed out that such intramolecular salts must be considered in addition to the ordinary forms.

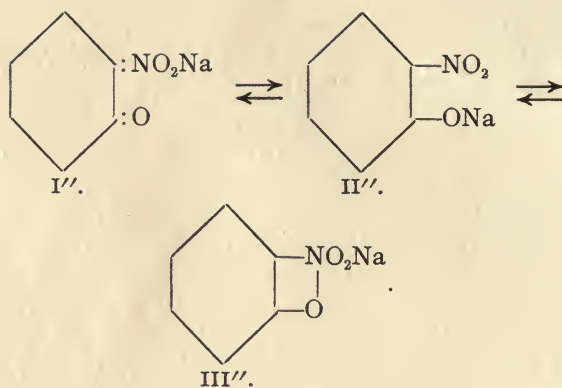
Hantzsch,<sup>4</sup> in working on this problem of the cause of color in salts, had to assume that both forms of the tautomeric acids are ionized, and consequently had to give up his former idea that a tautomeric acid exists in two forms, one of which, the pseudoacid, is not ionized, while the other, the "echt" acid, is dissociated. This led him then to assume the presence of two salts in equilibrium, instead of the one salt, that of the "echt" acid. But a new idea advanced by him was that there were not only *two* tautomeric salts of nitrophenol, for instance, but also another intramolecular salt, III'', analogous to III., with a different color and different properties:

<sup>1</sup> Ber. d. chem. Ges., **37**, 2333.

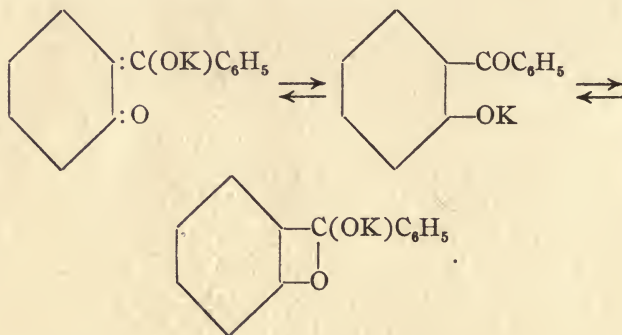
<sup>2</sup> Reinhardt: Dissertation, Erlangen, 1906.

<sup>3</sup> Amer. Chem. J., **31**, 187; **32**, 606, foot-note.

<sup>4</sup> Ber. d. chem. Ges., **39**, 1084; **40**, 333.



In another case Hantzsch<sup>1</sup> assumed the presence of such an intramolecular salt, analogous to III. He found that oxybenzaldehydes and oxybenzophenones yield different colored salts to which he gave the formulas



The chief reason, however, for believing that an intramolecular salt, III., is probably the chief source of color in the phenolphthalein series came from work by Jackson<sup>2</sup> and his coworkers, by Wichelhaus<sup>3</sup> and by Posner.<sup>4</sup> Jackson and Oenslager<sup>5</sup> and Clarke,<sup>6</sup> and also Wichelhaus, showed

<sup>1</sup> Ber. d. chem. Ges., **39**, 1084, 3080; **40**, 335, footnote, etc.

<sup>2</sup> Their articles did not bear especially on indicators.

<sup>3</sup> Ber. d. chem. Ges., **5**, 849.

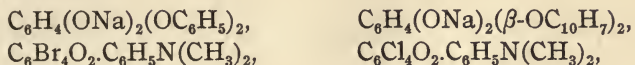
<sup>4</sup> Ann. Chem. (Liebig), **336**, 85.

<sup>5</sup> Amer. Chem. J., **18**, 1.

<sup>6</sup> *Ibid.*, **34**, 441.



that when a quinone adds sodium phenolate or sodium  $\beta$ -naphtholate, or dimethylaniline, the intensely colored double salts,



are formed in *nonaqueous* solvents. Posner ascribed to these compounds different constitutions, but that question does not affect the theory. It was therefore a question to be decided by experiment whether the quinone group and the sodium phenol group of II. might not also combine to form a deeply colored salt, III., even in *aqueous* solutions. But it was clear that the experiments would actually have to be done in aqueous solutions, in which the color changes of phenolphthalein manifest themselves, especially as Jackson found the quinonephenolate addition products to be decomposed by water.<sup>1</sup>

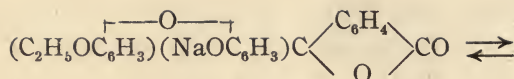
In a similar way it is clear that the phenol ester salt B, p. 126, can not be deeply colored. Since the phenol *esters* do not unite with quinones at all, the color of B is simply that of the quinone group.

If the theory of tautomeric salts is to explain the alkylation reactions and the color changes of phenolphthalein, etc., correctly, three things must be proved *quantitatively*, and to this part of the problem I have now devoted myself.

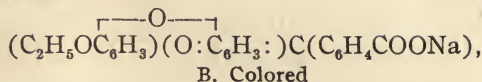
I. It must be proved by experiment that fluorescein forms the tautomeric dibasic salts, each of which yields, to some extent, its corresponding ester in independent side reactions, no ester being formed entirely by a rearrangement of another ester.

I have now been able to do this in a clear-cut way, as is brought out fully in the experimental portion. The phenol ethyl ester of fluorescein, for instance, forms a monosodium salt which is colored and which exists in the two forms in equilibrium with each other:

<sup>1</sup> Jackson and Oenslager: Amer. Chem. J., **18**, 16, 20.

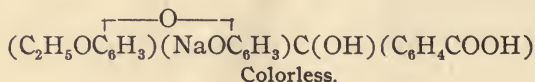


A. Colorless.

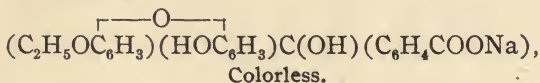


B. Colored

and with their hydrated forms,



Colorless.

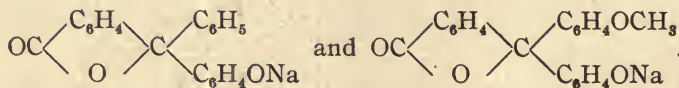


Colorless.

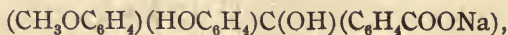
and perhaps with the intermolecular salts.

That there is not simply one salt, B, is proved by the fact that this sodium salt and ethyl iodide yield *two* diethyl esters, the colored quinone ester corresponding to B and the colorless diphenol ester corresponding to A. These esters do not rearrange into each other under the conditions of the experiment and hence at least two tautomeric salts must be present.

This theory of tautomeric salts accounts very nicely also for the *lack of color* in some of these salts. Such substances as *p*-oxydiphenylphthalid,<sup>1</sup> the phenol ethyl ester of phenolphthalein,<sup>2</sup> and the corresponding phenol ester of tetrabromophenolphthalein,<sup>3</sup> dissolve in alkalis without color. Since each of these compounds yields *only* the corresponding lactone ester I believe that the salts have to some extent the lactoid form,



This may be in equilibrium with the hydrated form,

<sup>1</sup> Baeyer: Ann. Chem. (Liebig), **354**, 171.<sup>2</sup> Ber. d. chem. Ges., **40**, 3728.<sup>3</sup> *Ibid.*, **30**, 177.

which Green and King<sup>1</sup> assumed to be the structure of all these colorless salts. But I do not think that this point of view of Green and King accounts for the formation of nearly quantitative yields of the phenol dimethyl ester from methyl iodide and the sodium salts of phenolphthalein and hydroquinonephthalein, of the phenyl methyl ester of dibrom-*p*-oxydiphenylphthalid from the sodium salt and methyl iodide, or for the formation of *both* isomeric esters of fluorescein obtained by me: my theory does account for these facts. Since Green and King assume the presence of a hydrated *carboxyl salt* we should certainly expect to obtain some carboxyl ester if their theory is correct; but no carboxyl ester is formed, apparently, from the colorless salts mentioned above. It is unfortunate that no one has isolated these colorless salts and shown by analysis whether they are hydrated and become colored when dehydrated, or whether the carboxyl esters rearrange into phenol esters. That these salts may actually exist in the lactoid form is proven, it seems to me, by the fact that Meyer and Spengler<sup>2</sup> actually made the colorless lactoid salts of the anilides of phenolphthalein and hydroquinonephthalein. This is a very important phase of my work and it will be continued in this laboratory from several points of view.

II. It must be proved that these *quinonephenolate double salts* of Jackson and Oenslager and of Wichelhaus and the *quiaminones* of Jackson and Clarke are formed in *aqueous solutions*. If these were decomposed completely into their constituents in water, it is evident that these substances could not be concerned in the color changes of indicators and dyestuffs as they are ordinarily used. I<sup>3</sup> have fortunately been able to prove that deeply colored compounds are formed by the union of benzoquinone or anthraquinone with salts of *o*-cresol, *p*-cresol, phenol, hydroquinone, pyrogallol and resorcinol, the colors of which disappear when acids are added. In fact such mixtures serve as very good indicators. Likewise, dimethylaniline or  $\alpha$ -dimethylamino-

<sup>1</sup> J. Chem. Soc., **85**, 398; Ber. d. chem. Ges., **40**, 3724.

<sup>2</sup> Ber. d. chem. Ges., **36**, 2949.

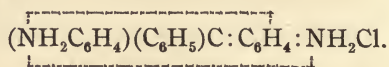
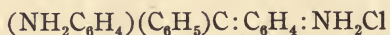
<sup>3</sup> Acree and Slagle: Amer. Chem. J., **39**, 534, 535.



$\alpha$ -bromnaphthalene and quinone form intensely colored *quinaminones* in aqueous solutions, the color of which fades to that of the quinone when the amine is converted into the salt.

This idea is further borne out by the fact that Bistrzycki's diphenylquinonemethane,<sup>1</sup> which can not form the quinonephenolate salt,  $(C_6H_5)_2C : C_6H_4 : O$ , is far less deeply colored than the salts of benzaurin,  $C_6H_5C( : C_6H_4 : O)(C_6H_4ONa)$ , or aurin,  $(NaOC_6H_4)_2C : C_6H_4 : O$ , which can form the intramolecular, deeply colored quinonephenolate group.

Further evidence is furnished by the brilliant work of Baeyer,<sup>2</sup> who showed that salts of *p*-aminotriphenylcarbinol,  $(C_6H_5)_2C : C_6H_4 : NH_2Cl$ , which can not form a *quinaminone*, are only light orange in color, whereas the *p,p*-diaminotriphenylcarbinol gives salts having an intense violet color because it forms, to some extent, the deeply colored *quinaminone* group:



When an excess of acids is added to fuchsin or to malachite green<sup>3</sup> the colors fade because the acid converts the amino group into a salt which can not form the quinaminone.

III. The equations and ideas used by Hantzsch and Stieglitz to express the affinity constant of the indicator and the tendency to form the colored salts are not complete<sup>4</sup> and have been replaced by those developed by Acree<sup>5</sup> to show the relations between the equilibrium constants and the affinity constants of the several tautomeric forms of the acid. These equations have been tested experimentally in the urazole series by Acree and Shadinger<sup>6</sup> and found to hold, and

<sup>1</sup> Ber. d. chem. Ges., **36**, 2337.

<sup>2</sup> Ann. Chem. (Liebig), **354**, 161-2.

<sup>3</sup> Acree and Slagle: Amer. Chem. J., **39**, 536.

<sup>4</sup> Acree: *Ibid.*, **39**, 529. Stieglitz: *Ibid.*, **39**, 652. Wegscheider: Z. Elek. Chem., **34**, 510. Hildebrand: J. Am. Chem. Soc., **30**, 1914.

<sup>5</sup> Amer. Chem. J., **38**, 11, *et seq.*, and many subsequent articles.

<sup>6</sup> *Ibid.*, **39**, 124.



similar ideas are also being used by Wegscheider. A great deal of quantitative work will be necessary to clear up all of these problems connected with the indicators. *The cause of the color<sup>1</sup> is probably the inter- or intramolecular change of the various salts into each other, as has been brought out thoroughly by Hartley and Baly.<sup>2</sup>*

In the last year or two a number of others have begun work from this point of view that the chief source of color is not the quinone group but a quinonephenolate group, and that the most important source of the color is probably the intramolecular salt formed by the union of the quinone and the phenolate or aniline derivative. In 1907, Baeyer<sup>3</sup> published a long and valuable article on the dyestuffs, in which he gave up his theory of halochromy in favor of the quinone theory, discussing fully his reasons for doing so. He proposed this quinonephenolate theory and tested it by treating fuchsone and fuchsonium chloride with sodium phenolate and dimethyl-*p*-toluidine, but no colors were obtained. My experiments, however, gave beautiful color changes.

Stieglitz<sup>4</sup> has also given up his former point of view and now has proposed the quinhydrone hypothesis as a cause of the color changes, including the salts as well.

Willstaetter and Piccard,<sup>5</sup> at about the same time, brought out in a valuable contribution the same quinhydrone hypothesis and applied it in a number of directions.

Recently K. H. Meyer<sup>6</sup> has discussed some of the recent work and ideas and prepared a number of compounds.

Since Acree's first paper was published R. Meyer<sup>7</sup> has presented an important article in which he has changed from Baeyer's theory of halochromy to the quinonephenolate theory which I am using.

Wegscheider<sup>8</sup> too has recently taken up the study of phenol-

<sup>1</sup> Amer. Chem. J., **39**, 537.

<sup>2</sup> J. Chem. Soc., **85**, 1029; **89**, 502, 514; **91**, 426, 1572.

<sup>3</sup> Ann. Chem. (Liebig), **354**, 162.

<sup>4</sup> Amer. Chem. J., **39**, 651.

<sup>5</sup> Ber. d. chem. Ges., **41**, 1458.

<sup>6</sup> *Ibid.*, **42**, 1149.

<sup>7</sup> *Ibid.*, **41**, 2446.

<sup>8</sup> Z. Elek. Chem., **34**, 510.

phthalein from a similar point of view and has obtained results in harmony with this theory.

It is evident then that a number of men have been engaged on work which led them to the same general point of view, which is a very great advance in the theory of indicators and dyestuffs. I do not claim any credit for the very important view advanced by Baeyer, Stieglitz, and Willstaetter that *quinhydrones*, as they are always defined, are concerned in the colors of the free acids. But I do believe that this theory of tautomeric salts accounts more fully for the *colors* of the *salts* and their *alkylation reactions* than the theory of any other worker, and since the salts are the substances of chief importance in the colors and reactions of dyestuffs, the free acids or bases being comparatively insignificant in this respect, I shall devote my attention chiefly to this phase of the subject.

A study of the affinity constants of the indicators from this point of view, of the influence of alcohol in decolorizing the salts, of the influence of salts and acids in intensifying the colors of the dyestuffs,<sup>1</sup> and other problems mentioned in my first article are of very great importance. The salts of weak bases, such as  $\text{SnCl}_2$ ,  $\text{AlCl}_3$ , etc., and also acids, seem to form deeply colored double compounds with a number of quinoid and lactoid derivatives. I suspect that in all such cases the basic properties of the oxygen of a quinone group are directly concerned.

#### FLUORESC EIN.

The melting point method can not be used as a criterion of the purity of fluorescein. It decomposed above  $290^\circ$  without melting. Every precaution was therefore taken in the preparation to obtain a pure substance. Pure phthalic anhydride and pure resorcinol were heated with zinc chloride at  $180^\circ$ . The product was obtained free from resorcinol by washing with several liters of cold water, and was then dissolved in a solution of sodium carbonate and precipitated by sulphuric acid. The fluorescein obtained in this way is

<sup>1</sup> K. H. Meyer: Ber. d. chem. Ges., **41**, 2568. Meyer and Hantzsch: *Ibid.*, **40**, 3479.

bright yellow in color. After it is crystallized a number of times from alcohol it becomes dark red, a darker red than sulphophenolphthalein. When the yellow product is heated in an air bath for five hours at  $115^{\circ}$  it shows no appearance of red whatever. This bright yellow color is retained even after standing in a glass-stoppered bottle eighteen months.

#### *The Four Ethyl Esters of Fluorescein.*

The four ethyl esters of fluorescein were obtained by dissolving fluorescein in alcoholic sodium hydroxide, adding ethyl iodide, and heating under a reflux condenser on the water bath. Different amounts of fluorescein, solvent, and halide were used and the time of alkylation varied from four to twenty-four hours. No definite conclusions were reached as to the amounts of the different esters formed under the different conditions. The best yield of esters, however, was obtained by continuing the alkylation eight hours.

After the reaction was over any excess of ethyl iodide was expelled by evaporation and the product was poured into cold water, whereupon the two diethyl esters were precipitated. These were then filtered and carbon dioxide was passed into the filtrate. This precipitated the two monoethyl esters.

The only method found for separating the two monoethyl esters was fractional crystallization from dilute alcohol. After repeated crystallizations the colored carboxyl ester, somewhat more soluble in dilute alcohol than the colorless phenol ester, was obtained with a constant melting point  $247^{\circ}$ . The colorless phenol ester was found to melt, when pure, at  $251^{\circ}$ .

The colored diethyl ester was separated from the colorless diethyl ester also by fractional crystallization from dilute alcohol. When pure, the colorless diethyl ester melts at  $182^{\circ}$ , and the colored diethyl ester at  $159^{\circ}$ .

As stated above, Herzig and Pollak, on methylating fluorescein salts with *methyl iodide*, obtained chiefly the lactoid esters. I have found, in general, that *ethyl iodide* also produces the lactoid esters in excess, although the ratio of the lactoid to the quinoid varies greatly with the conditions of the experiment and time of alkylation. Quite different



results were obtained with *diazomethane*; Herzig and Pollak obtained with this reagent chiefly the quinoid esters.

I have found that *diazoethane* yields, with an excess of either the red and yellow fluorescein, only the colored quinoid diethyl ester. The product of the reaction, without purification, melts at  $157^{\circ}$ , only two degrees below the melting point of the pure ester,  $159^{\circ}$ . When this ester is crystallized from glacial acetic acid it gives the proper melting point.

*Preparation of the Pure Sodium Salt of the Phenol Ethyl Ester of Fluorescein.*

The pure sodium salt of the phenol ethyl ester was prepared by agitating an excess of the ester with a solution of sodium hydroxide and then filtering the undissolved ester. The filtrate was shaken again with a little of the ester and filtered. The filtrate was extracted with carbon tetrachloride and then evaporated to dryness on the water bath. There is no loss in weight on evaporating this salt to dryness on the water bath, although some of the esters are slightly volatile under these conditions.

The sodium salt of the phenol ester dissolves in water with a color much less intense than that of the fluorescein salt, and in ethyl and methyl alcohol with a very faint color at temperatures from  $-15^{\circ}$  to  $0^{\circ}$ . This color increases very decidedly as the temperature is raised to  $80^{\circ}$ , but decreases again as the temperature is lowered.

An attempt was made to study the velocity of ester formation; the equation for the reaction is that of the second order

$$\frac{x}{t(A-x)} = AK.$$

The concentrations of the sodium salt and ethyl iodide were 0.3 weight normal and volume normal, respectively, in 40 per cent alcohol.

The solution was sealed in a tube and heated in a constant temperature bath at  $60^{\circ}$ .

In the following table  $t$  gives the time in hours,  $A$  the number of grams of salt taken,  $x$  the amount of ester formed,

and  $A-x$  the amount of unchanged salt.  $AK$  is the constant calculated for a bimolecular reaction.

$t$ .	$A$ .	$A-x$ .	$x$ .	$AK$ .
2	0.382	0.3169	0.0651	0.10
3	"	0.3053	0.0767	0.19
4	"	0.2492	0.1328	0.13
7	"	0.2028	0.1792	0.12
(17)	"	0.0190	0.3630	0.11
(24)	"	0.0544	0.3276	(0.25)

The divergence of  $AK$  from a constant value is due to the difficulty in obtaining quantitative methods of separation and analysis.

I found that on ethylating the sodium salt as above, a mixture of the colorless phenol diethyl ester and the colored quinone diethyl ester is formed. To separate and identify these esters I boiled the alkylation product about three hours in alkali, which saponified the colored quinone diethyl ester. The solution was then filtered, the filtrate acidified, the phenol ethyl ester extracted with carbon tetrachloride, and identified by its melting point,  $247^{\circ}$ .

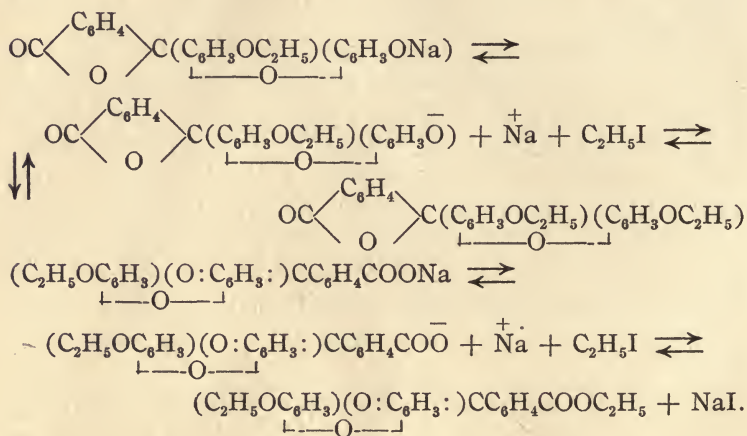
The unsaponified colorless phenol diethyl ester was collected from the filter and identified by the melting point,  $251^{\circ}$ .

In order to determine whether any rearrangement of the esters took place under the conditions of the experiment, I dissolved 0.0524 gram of the colorless phenol ester and 0.5500 gram of the colored quinone ethyl ester in 5 cc. of 40 per cent alcohol with ethyl iodide in 0.3 N solution of 40 per cent alcohol and heated the mixture a number of hours in a sealed tube in the bath at  $60^{\circ}$ . The tube was then opened and after separation 0.0516 gram of the colorless phenol ethyl ester and 0.5494 gram of the colored quinone ethyl ester were recovered. I then dissolved 0.6024 gram of the sodium salt of the phenol ethyl ester, 0.0316 gram of the colorless phenol ethyl ester, and 0.1702 gram of the colored quinone ethyl ester in 40 per cent alcohol, sealed this solution in a tube, and heated at  $60^{\circ}$  for six hours. The tube was then opened and the esters extracted from the salt. After

the separation 0.0306 gram of the colorless phenol ethyl ester and 0.1698 gram of the colored quinone ethyl ester were recovered.

*Conclusions from the Alkylations.*

Since the colorless phenol diethyl ester and the colored quinone diethyl ester are formed from the sodium salt of the phenol ethyl ester and since we have found that no rearrangement takes place under the conditions of the experiment, the equilibrium and reactions can be expressed as follows:



The equilibrium is assumed to be between the molecular forms of the salts because the evidence obtained in work on the urazoles seems to point in this direction. The same is true of the assumption of a reaction between the alkyl halide and the anions of the salt. It has been shown in work in other fields that reaction mechanisms are sometimes very complex and I do not commit myself finally as to the above assumptions.

PHENOLPHTHALEIN.

Phenolphthalein was obtained quite pure, melting at  $254^\circ$ , by the method of McCoy.<sup>1</sup>

<sup>1</sup> Amer. Chem. J., **31**, 507.



The attempt to obtain the four esters of phenolphthalein in sufficient quantity and purity by direct alkylation of phenolphthalein in alkaline solution with ethyl iodide proved fruitless. The potassium salt of phenolphthalein was treated with sulphonyl chloride. The reaction was vigorous, sulphur dioxide being evolved. The product of the reaction, resembling tar, was readily soluble in ether and gave a purple color with alkali but was not obtained pure.

#### TETRABROMPHENOLPHTHALEIN.

Since the tetrabromphenolphthalein and its derivatives were more readily obtained pure, attention was directed to them.

Phenolphthalin was prepared according to the directions of Baeyer.<sup>1</sup> This can be obtained quite free from phenolphthalein by crystallization from boiling water: 100 parts of water dissolve at 20° 0.0175 parts of phenolphthalin. When pure it melts at 225° and dissolves in alkali entirely without color. It is not changed appreciably on standing, but by prolonged heating in air it is oxidized to phenolphthalein.

In all of the following solubility experiments a known quantity of the acid or ester was shaken in a machine with a known quantity of alkali, not sufficient for solution, at 20°, for a number of hours. The undissolved acid or ester was filtered and weighed. The filtrate was acidified and the precipitated material also weighed as a check.

Meyer and Spengler<sup>2</sup> found that the unsubstituted phthaleins neutralize two molecular equivalents of alkali. My results with the phthaleins verify this. But the phthalins require, in general, somewhat less than two molecular equivalents of alkali, instead of the calculated three molecules, a proof that the phthalins are much weaker acids whose salts are more greatly hydrolyzed. Since it is proposed to measure the affinity constants of a large number of these dyestuffs a preliminary study of the hydrolysis constants through a de-

<sup>1</sup> Ann. Chem. (Liebig), **202**, 80.

<sup>2</sup> Ber. d. chem. Ges., **38**, 1327.



termination of the solubilities of these substances in alkalis seemed desirable.

*Solubility of Phenolphthalin in Alkali.*

Amount of acid dissolved.	Calculated cc. of 0.1 N NaOH, one molecular equivalent to one of acid.	cc. of NaOH required.
1.3205	41.3	29.22
0.4901	15.3	10.78

The small amount of alkali required for the solution of phenolphthalin can be explained by the formation of an acid salt in solution.

I prepared tetrabromphenolphthalin by Baeyer's method.<sup>1</sup> It crystallizes from benzene in colorless short needles which melt at 208°–209°. When exposed to the light in a glass-stoppered bottle for several months it becomes colored light pink, without, however, any change in the melting point.

*Solubility of Tetrabromphenolphthalin in Alkali.*

Amount of acid dissolved.	Calculated cc. of 0.1 N NaOH, two molecular equivalents to one of acid.	cc. of NaOH required.
0.7614	9.12	7.48
0.4731	7.06	5.49

It appears from this experiment that an acid salt is formed in this case.

The carboxyl ester of phenolphthalin was obtained by passing hydrogen chloride into an alcoholic solution of the acid. This ester crystallizes from dilute alcohol in colorless leaves which melt at 157°–158°. The ester is quite stable, being saponified only to a slight extent by standing overnight in a ten per cent solution of sodium hydroxide.

The carboxyl ester of phenolphthalin was brominated by dissolving it in glacial acetic acid and adding bromine. The tetrabrom product crystallizes from glacial acetic acid and melts at 164°.

<sup>1</sup> *Ann. Chem. (Liebig)*; **202**, 85.



*Solubility of the Carboxyl Ethyl Ester of Tetrabromphenolphthalin in Alkali.*

Amount of acid ester dissolved.	Calculated cc. of 0.1 N NaOH, two molecular equivalents to one of acid ester.	cc. NaOH required.
0.4804	14.46	15.95
0.3160	9.52	10.58

I found that potassium dichromate had no oxidizing effect on this ester. Potassium permanganate and potassium ferricyanide readily oxidize it to the salt of the carboxyl ester of tetrabromphenolphthalein. The free ester was not obtained from this salt in sufficient quantity and purity for the investigation.

I prepared *p*-oxy-*o*-benzoylbenzoic acid according to Friedländer's directions,<sup>1</sup> and the carboxyl ethyl ester by passing hydrogen chloride into the alcoholic solution. The ester crystallizes from glacial acetic acid as a white crystalline powder melting at 115°.

I attempted to bring about the condensation of this ester with phenol in the presence of zinc chloride and also of concentrated sulphuric acid in order to obtain the carboxyl ethyl ester of phenolphthalein, but was unsuccessful.

The attempt to prepare the silver salts of the carboxyl ethyl ester of phenolphthalein and the carboxyl ethyl ester of tetrabromphenolphthalein proved a failure. A water solution of silver nitrate was added to a water solution of each salt at 0° in a vessel of actinic glass, but in each case silver oxide separated and no trace of the silver salt was formed.

*p*-OXYDIPHENYLPHTHALID.<sup>2</sup>

*p*-Oxydiphenylphthalid,  $\text{OC} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C} \begin{array}{c} \diagup \text{C}_6\text{H}_5 \\ \diagdown \text{C}_6\text{H}_4\text{OH} \end{array}$ , should, from the theory, yield one colorless ester and one colorless salt.

This substance was prepared according to Baeyer's method, by condensing phenol and benzoylbenzoic acid with concen-

<sup>1</sup> Ber. d. chem. Ges., 26, 172.

<sup>2</sup> Ann. Chem. (Liebig), 354, 162.

trated sulphuric acid and crystallizing the product from glacial acetic acid. It melted at  $164^{\circ}$ .

*Solubility of  $p$ -Oxydiphenylphthalid in Alkali.*

Amount of acid dissolved.	Calculated cc. of 0.1 N NaOH, one molecular equivalent to one of acid.	cc. NaOH required.
0.1044	3.46	11.34
0.0700	2.32	7.28

That this acid is extremely weak and the salt highly hydrolyzed is shown by the excess of alkali above the calculated required for solution.

The sodium and potassium salts of  $p$ -oxydiphenylphthalid are precipitated from a water solution by the addition of an excess of a concentrated solution of sodium or potassium hydroxide but it was found impossible to obtain either of these salts for analysis free from alkali. The attempt to isolate other metallic salts also proved futile.

A colorless oil was formed by heating a solution of the  $p$ -oxydiphenylphthalid in absolute alcohol with sodium wire but was not obtained pure. No salt was formed on boiling a solution of the acid in anhydrous ether with sodium wire for five hours.

I experienced the same difficulty in attempting to isolate the alkali salts of benzo- $p$ -cresophthalein.

On methylating  $p$ -oxydiphenylphthalid with methyl iodide and alcoholic sodium hydroxide a colorless ester was obtained, but not in pure condition.

**DIBROM- $p$ -OXYDIPHENYLPHTHALID.**

$p$ -Oxydiphenylphthalid was dissolved in glacial acetic acid, at about  $60^{\circ}$ , and a solution of bromine in glacial acetic acid was added. On cooling the solution, the dibrom- $p$ -oxydiphenylphthalid separated out. On crystallization from acetic acid this was obtained pure in white crystals which melt at  $199^{\circ}$ .

The methyl ester prepared with diazomethane gave on analysis the following results:



	Calculated for $C_{21}H_{16}O_3Br_2$ .	Found. (Carius method.)
Br. . . . .	33.75	I. 33.48 II. 33.24

Dibrom-*p*-oxydiphenylphthalid was methylated by alcoholic sodium hydroxide and methyl iodide. The methyl ester was obtained as a white powder which crystallizes readily from glacial acetic acid and melts at  $157^\circ$ .

By methylating the dibrom-*p*-oxydiphenylphthalid with diazomethane an identical ester was obtained, melting at  $157^\circ$ . No lowering of the melting point was produced on fusing a mixture of these esters.

These experiments seem to prove very clearly that the sodium salt and the free acid have the same constitution, that of the lactoid form, and give evidence that the theory of tautomeric salts is correct.

#### EXPERIMENTS WITH THE DILATOMETER.

It seemed likely that the affinity constants of these weak acids might be determined by the use of the dilatometer,<sup>1</sup> provided no salt effect interferes. This method depends on the reversible reaction involved in the condensation of acetone, and the splitting of the diacetone alcohol thus formed into two molecules of acetone. The expansion of the solution due to the change of the diacetone is generally measured. This reaction is catalyzed by the presence of hydroxyl ions and the velocity is proportional to the concentration of these ions.

The diacetone alcohol was prepared by extracting pure calcium hydroxide in a Soxhlet extractor with acetone, according to Hofmann's method. The solution was freed from water and acetone by distilling it under diminished pressure and was then fractionated. The solutions measured contained from two to ten per cent of the diacetone alcohol in conductivity water. A solution of diacetone alcohol in conductivity water showed no appreciable change after standing several months. The measurements were made in a constant tem-

<sup>1</sup> Koelichen: Z. physik. Chem., **33**, 132.

perature bath at 25°. The variation during the experiment was only 0°.01.

Velocity constants for sodium hydroxide having a concentration of N/10, N/20, N/40, N/80, and N/160 in the dilatometer were obtained from the equation for the reaction of the first order,  $\frac{A}{t(A-x)} = K$ . The results are given in Tables I.-V., inclusive.

Equal volumes of ten per cent diacetone alcohol and alkali of the proper strength to give the above concentrations were used. In the tables  $t$  is the time in minutes,  $A$  the total expansion in divisions on the dilatometer stem, and  $K$  the velocity constant.

Table I.—0.1 N Sodium Hydroxide.  $A = 68.1$ .

$t$ .	$A-x$ .	$K$ .	$t$ .	$A-x$ .	$K$ .
10	40.0	0.0224	30	14.2	0.0224
15	30.8	0.0226	40	8.4	0.0225
20	24.2	0.0221	50	4.8	0.0224
25	18.4	0.0223			

Mean, 0.0224

Table II.—0.05 N Sodium Hydroxide.  $A = 36.0$ .

$t$ .	$A-x$ .	$K$ .	$t$ .	$A-x$ .	$K$ .
5	31.3	0.0119	50	9.6	0.0115
15	23.9	0.0116	55	8.5	0.0114
25	18.4	0.0117	85	3.8	0.0114
35	13.9	0.0118			

Mean, 0.0116

Table III.—0.025 N Sodium Hydroxide.  $A = 44.2$ .

$t$ .	$A-x$ .	$K$ .	$t$ .	$A-x$ .	$K$ .
30	29.5	0.00585	100	12.0	0.00575
40	25.7	0.00589	120	9.4	0.00572
60	20.0	0.00574	150	6.4	0.00577
80	15.5	0.00571			

Mean, 0.00578

Table IV.—0.0125 N Sodium Hydroxide.  $A = 41.2$ .

$t$ .	$A-x$ .	$K$ .	$t$ .	$A-x$ .	$K$ .
10	38.6	0.00273	100	22.6	0.00271
30	34.2	0.00270	130	19.0	0.00269
50	30.2	0.00270	160	16.0	0.00270
70	27.3	0.00270			

Mean, 0.00270

Table V.—0.00625 N Sodium Hydroxide.  $A = 48.0$ .

$t$ .	$A-x$ .	$K$ .	$t$ .	$A-x$ .	$K$ .
20	45.5	0.00117	200	29.0	0.00119
50	41.9	0.00118	260	24.8	0.00110
80	38.9	0.00116	320	21.5	0.00119
140	33.5	0.00112			
Mean, 0.00116					

*Dilatometer Measurements of Solutions of Phenolphthalein.*  
 —The pure sodium salt of phenolphthalein was prepared by shaking an excess of the acid with alkali a number of hours and carefully filtering out the excess of acid. A portion of the filtrate containing 0.400 gram of the disodium salt was placed in the dilatometer with an equal volume of ten per cent diacetone alcohol. In Tables VI. and VII.,  $A$  has been calculated only approximately from a number of experiments.

Table VI.— $A = 100$ .

$t$ .	$A-x$ .	$K$ .	$t$ .	$A-x$ .	$K$ .
1480	92.6	0.000022	3280	83.5	0.000023
1900	89.6	0.000022	4150	80.8	0.000022
2620	87.6	0.000023	4900	78.1	0.000021
Mean, 0.000022					

Table VII.— $A = 100$ .

$t$ .	$A-x$ .	$K$ .	$t$ .	$A-x$ .	$K$ .
960	92.9	0.000023	3420	83.6	0.000022
1830	90.2	0.000023	4080	80.6	0.000022
2250	89.4	0.000021	6140	69.2	0.000024
Mean, 0.000022					

This volume for  $K_{trans}$  corresponds to a hydroxyl ion concentration of 0.00012 N. If we take as the concentration of the phenolphthalein in saturated solution the value 0.0012 N found by McCoy<sup>1</sup> and remember that the solution of the phenolphthalein salt is diluted with an equal volume of the solution of diacetone alcohol, we should obtain  $2 \times 10^{-7}$  for the hydrolysis constant, or  $0.6 \times 10^{-7}$  for the affinity constant of phenolphthalein. This is much larger than the values ob-

<sup>1</sup> Amer. Chem. J., 31, 511.



tained by Salm, McCoy, Hildebrand, and Wegscheider and shows most decidedly, as do Tables VIII. to XI., inclusive, that the phenolphthalein salt lowers the catalytic effect of the hydroxyl ions very materially. Unless some means can be found to obviate this the method can not be used to determine the affinity constants of these indicators and related compounds.

Solutions of phenolphthalein were then prepared by dissolving a definite amount of the acid in a sodium hydroxide solution containing varying amounts of the alkali. Dilatometer measurements were made with these solutions. The results are given in Tables VIII. to XI., inclusive. It is seen that the velocity constant decreases with increase in the amount of phenolphthalein present.

In the following tables, the amounts of alkali used are expressed in molecular equivalents for one molecular equivalent of acid:

*Table VIII.—4.6 N/40 NaOH.  $A = 50.5$ .*

<i>t.</i>	<i>A—x.</i>	<i>K.</i>	<i>t.</i>	<i>A—x.</i>	<i>K.</i>
10	45.9	0.00424	60	28.2	0.00421
20	41.6	0.00420	80	22.8	0.00421
30	37.8	0.00429	120	15.4	0.00429
40	34.2	0.00423			

Mean, 0.00424

*Table IX.—20 N/10 NaOH.  $A = 34.2$ .*

<i>t.</i>	<i>A—x.</i>	<i>K.</i>	<i>t.</i>	<i>A—x.</i>	<i>K.</i>
8	24.2	0.0187	24	12.1	0.0187
12	20.3	0.0188	28	10.2	0.0187
16	17.1	0.0187	36	7.2	0.0187
20	14.5	0.0186			

Mean, 0.0187

*Table X.—40 N/10 NaOH.  $A = 28.8$ .*

<i>t.</i>	<i>A—x.</i>	<i>K.</i>	<i>t.</i>	<i>A—x.</i>	<i>K.</i>
12	15.9	0.0215	28	7.3	0.0212
15	13.8	0.0213	38	4.5	0.0212
20	10.9	0.0210	49	3.4	0.0210
24	8.9	0.0212			

Mean, 0.0212



Table XI.—70 N/20 NaOH.  $A = 34.3$ .

<i>t.</i>	<i>A</i> — <i>x.</i>	<i>K.</i>	<i>t.</i>	<i>A</i> — <i>x.</i>	<i>K.</i>
5	30.0	0.0116	30	15.9	0.0110
10	26.5	0.0112	40	11.5	0.0118
15	23.1	0.0114	50	9.6	0.1009
20	20.6	0.0110			
Mean, 0.0113					

*Dilatometer Measurements of Solutions of p-Oxydiphenyl-phthalid.*

These solutions were prepared by dissolving the acid in varying amounts of caustic soda. The results of the dilatometer measurements are given in Tables XII. to XIV., inclusive. The same salt catalysis is noticed in this case as with phenolphthalein. This salt catalysis was noticed by Koelichen, who found that some salts acted as negative and others as positive catalyzers.

Table XII.—20 N/10 NaOH.  $A = 34.8$ .

<i>t.</i>	<i>A</i> — <i>x.</i>	<i>K.</i>	<i>t.</i>	<i>A</i> — <i>x.</i>	<i>K.</i>
8	28.3	0.0112	40	12.4	0.0111
16	23.2	0.0110	56	8.2	0.0112
24	18.7	0.0112	72	5.3	0.0113
32	15.3	0.0111			
Mean, 0.0112					

Table XIII.—40 N/10 NaOH.  $A = 32.3$ .

<i>t.</i>	<i>A</i> — <i>x.</i>	<i>K.</i>	<i>t.</i>	<i>A</i> — <i>x.</i>	<i>K.</i>
5	25.3	0.0212	30	7.7	0.0218
10	19.9	0.0210	40	7.7	0.0218
15	15.5	0.0212	60	2.0	0.0217
20	11.8	0.0218			
Mean, 0.0215					

Table XIV.—80 N/10 NaOH.  $A = 33.6$ .

<i>t.</i>	<i>A</i> — <i>x.</i>	<i>K.</i>	<i>t.</i>	<i>A</i> — <i>x.</i>	<i>K.</i>
5	25.8	0.0229	25	9.0	0.0227
10	19.9	0.0227	30	7.0	0.0228
15	15.1	0.0229	40	4.0	0.0229
20	11.7	0.0229			
Mean, 0.0228					

The above results for the various concentrations of sodium hydroxide, phenolphthalein, and *p*-oxydiphenylphthalid are shown in Fig. I., plotted in the form of a curve.

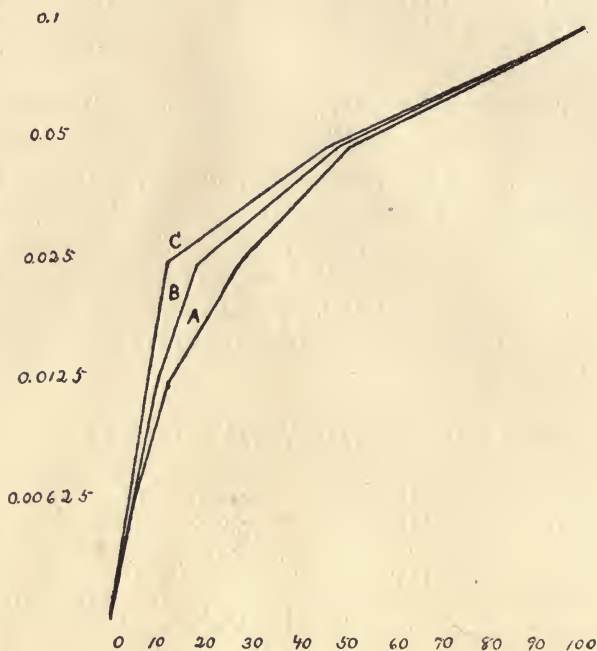


Fig. I.

The abscissas represent the velocity constants,  $K$ , and the ordinates the normality of the original alkaline solutions. Curve A shows the results for sodium hydroxide (the deviation of A from a straight line is, of course, due to the suppressed ionization at the higher concentrations); curve B shows the results obtained with the phenolphthalein solutions; and C, those obtained with solutions of *p*-oxydiphenylphthalid. The decrease in the velocity constant due to the presence of the phthalein or phthalid salt is very clearly shown, the decrease being greater in the case of *p*-oxydiphenylphthalid, C, than in the case of phenolphthalein, B.

*A New Dilatometer.*

It is readily seen that the glass dilatometer as devised by Koelichen is not sufficiently sensitive for studying very dilute solutions of alkali nor for the very accurate investigation of this salt catalysis. An attempt was made to obtain a more sensitive instrument by following the plan used by Prof. Morse in his work on osmotic pressure.

A brass cell (Fig. II.) was made, with a capacity of 25 cc. and an internal diameter of 17 mm., the wall being 2 mm. thick. The cell was uniformly nickel-plated inside and outside. It was closed by a brass cone (*b*) into which was fastened with Wood's metal (*c*) an open manometer tube, etched in 1 mm. divisions, and having a bore of 0.5 mm. diameter. A small platinum tube (*d*) opening within the cell, by the side of the manometer, was also fastened into the cone. This small tube could be closed with a screw cap (*e*).

The cap was used to regulate the height of the liquid in the manometer before the measurements were taken. When a measurement was to be taken the manometer tube was filled with pure water. The diacetone alcohol and alkaline solution were brought to the proper temperature, thoroughly mixed, and then poured into the cell. The cone containing the manometer was then quickly placed in the cell and tightened by the threaded brass collar (*g*). The superfluous liquid was allowed to escape from the small platinum tube until the meniscus was at the proper height in the manometer tube and the screw cap was then tightly closed. It was found impracticable to use washers of any kind between the cone and the cell at (*f*), as their slightest contraction or expansion caused a change in the volume of the cell and hence an error in reading. A watertight connection was obtained at this point (*f*) by the use of a thin layer of a mixture of vaseline and the lubricant obtained by melting together rubber and paraffine.

During the measurements, which lasted from three to nine hours, the instrument was immersed so that the meniscus was at a constant level in a constant temperature bath. The

temperature must be carefully regulated as a change of more than  $0^{\circ}.005$  of a degree causes considerable error in reading.

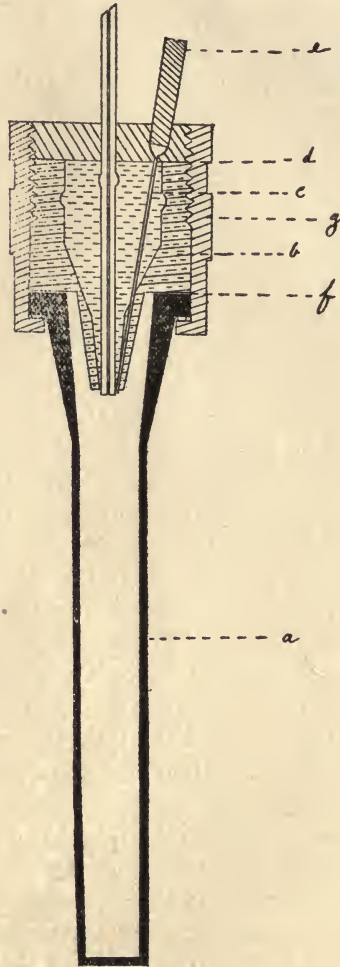


Fig. II.

A number of improvements have suggested themselves while working with this instrument, yet the advantages of the present type over the glass dilatometer are evident. This



cell, when placed in the bath, will attain temperature equilibrium in two to three minutes. The following tables will show the degree of accuracy that can be attained. In these measurements a 2 per cent solution of diacetone alcohol was used.

Table XV.—0.0483 N Sodium Hydroxide.  $A = 14.29$ .

<i>t.</i>	$A-x.$	$K.$	<i>t.</i>	$A-x.$	$K.$
2	13.57	0.01123	31	6.41	0.01125
4	12.89	0.01120	41	4.95	0.01120
6	12.23	0.01126	51	3.83	0.01123
21	9.32	0.01121	61	2.95	0.01126
26	7.13	0.01126			

Mean, 0.01123

Table XVI.—0.0227 N Sodium Hydroxide.  $A = 22.80$ .

<i>t.</i>	$A-x.$	$K.$	<i>t.</i>	$A-x.$	$K.$
10	20.10	0.005673	35	14.50	0.005670
15	18.39	0.005677	50	11.92	0.005671
20	17.63	0.005679	60	10.46	0.005672
25	16.52	0.005672	70	9.18	0.005672
30	15.47	0.005678			

Mean, 0.005675

These are remarkably good constants and serve to show how accurate our chemical methods can be made. Doubtless many other reactions can be studied by such methods and it is hoped that this work will be continued.

### BIOGRAPHICAL.

Edgar Apple Slagle was born at Cessna, Bedford Co., Pa., February 19, 1883. He received his preliminary education at the private school of Miss Martha E. Grove, Hanover, Pa. He was graduated from Mercersburg Academy, Mercersburg, Pa., in the Latin Scientific course, in June, 1901, and from Franklin and Marshall College, Lancaster, Pa., with the degree of Ph.B., in June, 1904.

In October, 1904, he entered Johns Hopkins University as a graduate student in Chemistry, his subordinate subjects being Physical Chemistry and Physics.

During the years 1905-1906 and 1906-1907 he was absent from the University instructing in Chemistry at Maryland College. During 1908-1909 he held the position of laboratory assistant to Prof. Renouf at Johns Hopkins University.









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